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# Structural dynamics of gas-phase molybdenum nanoclusters: A transmission electron microscopy study

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In this paper we study structural aspects of molybdenum clusters by transmission electron microscopy. The deposited clusters with sizes 4 nm or larger show a body-centered crystal (bcc) structure. The clusters are self-assembled from smaller structural units and form cuboids with a typical size of 4 nm or larger. With reducing cluster size, the face-centered crystal (fcc) structure appears due to dominance of surface energy minimization, while self-assembly into large cuboids with sizes up to 30 nm is still observed. Our observation implies that the basic building blocks of large cuboids are actually not smaller cubes. Annealing leads to cluster coalescence at temperatures  $\sim 800^\circ\text{C}$ , with the crystal habit changing to truncated rhombic dodecahedron for isolated clusters, while the large cuboidally shaped particles become more faceted polyhedra. © 2005 American Institute of Physics. [DOI: 10.1063/1.1886261]

Materials built up from nanostructure constituents can have fundamentally different properties than conventional materials.<sup>1–5</sup> Size-dependent effects can be expected to appear when the building blocks are smaller than a certain critical dimension. In addition, interfaces play a major role in thin films derived from nanosized clusters. Although the structural studies on metal clusters consisting of  $<10^1$  atoms are numerous,<sup>6</sup> those on metallic clusters with between  $10^1$  and  $10^4$  atoms are relatively few. In general the particles have the form of polyhedra with various degrees of truncation since these shapes will lead to surface energy minimization for particles formed at equilibrium, or because of kinetics where the shape is determined by the rate at which different crystal faces grow. The combination of factors such as temperature, kinetics, impurities, and surface energy effects can lead to extraordinary nanoparticle shapes and size distributions.<sup>5</sup>

Because the metal clusters carry a relatively large surface energy, they can have a structure different from the bulk in order to lower the surface energy. It has been predicted that metal clusters with a bulk bcc structure would have a fcc structure for a small number of cluster atoms.<sup>7,8</sup> More specifically, x-ray diffraction experiments with molybdenum clusters have shown that a structural evolution occurs from amorphous  $\rightarrow$  fcc  $\rightarrow$  bcc structure as the number of constituent atoms increases.<sup>9</sup> It has been proposed that Mo clusters can have either the A15 or bcc structure.<sup>5</sup> In general, the crystal habit for clusters with a bcc structure has been suggested to be the truncated rhombic dodecahedron,<sup>5</sup> including many elements such as Mo, Nb, Fe, V, and Cr.<sup>5,10</sup> In addition, self-arrangement of individual particles into larger cubes made out of  $3 \times 3 \times 3$  smaller cubic particles has been reported in the case of Mo.<sup>11,12</sup> Existing within a narrow size distribution, collisions between 5.5 nm Mo cubes have also been investigated.<sup>11,12</sup> When the Mo cubes collided, they became self-organized into  $2 \times 2 \times 2$ ,  $3 \times 3 \times 3$ , and  $4 \times 4 \times 4$  arrangements of the smaller 5.5 nm cubes.<sup>11,12</sup> It has been

suggested that contact of the cubes leads to a lower surface energy so as to explain the self-organization into larger cubes (Fig. 1).

In this article we present results on the structural evolution of molybdenum metal nanoclusters as a function of cluster size at room temperature as-deposited, and during high temperature annealing. We show evidence that the structural unit that composes the self-assembled cuboids does not have a perfectly cubic crystal habit. The clusters were produced with a NC200U nanocluster source from Oxford Applied Research Ltd. (<http://www.oaresearch.co.uk>). Metal atoms were sputtered from a pure Mo target and condensed into clusters in an argon-filled aggregation region (Ar pressure  $\sim 0.1$  mbar). To make clusters smaller than 3 nm, a He drift gas was introduced in addition to the Ar. The clusters were deposited onto silicon nitride membranes of thickness 10 nm for analysis in a JEOL 2010F transmission electron microscope. *In situ* annealing in TEM offers the unique possibility of monitoring not only changes in cluster size due to coalescence, but also in crystal structure, habit, and oxide coverage as a function of temperature in real time.

The as-deposited Mo nanoclusters have a bcc crystal structure for cluster diameters  $D > 4$  nm, while for smaller cluster sizes a fcc crystal structure is formed (Fig. 2). The absence of oxide, either with bcc or fcc structure (despite their exposure to air during sample transfer to TEM) was confirmed by electron diffraction and electron energy loss spectroscopy. For the small clusters [Fig. 2(a)], the measurement from the Fourier transform [Fig. 2(b)] yields a lattice spacing 0.213 nm for the (200) planes and 0.242 nm for the (111) planes. The latter yields a ratio 1.14 which is comparable to a fcc ratio of  $2/\sqrt{3}$  ( $\approx 1.16$ ). For nanoclusters of 1460–3900 atoms, the structural transitions between fcc to bcc have been shown to take place.<sup>9</sup> In our case we observe such a change for clusters sizes around 3 nm. Note that the fcc structure is more compact than the bcc structure and that the fcc structure provides a lower surface energy, and eventually at small sizes a lower cluster energy than the bcc structure.

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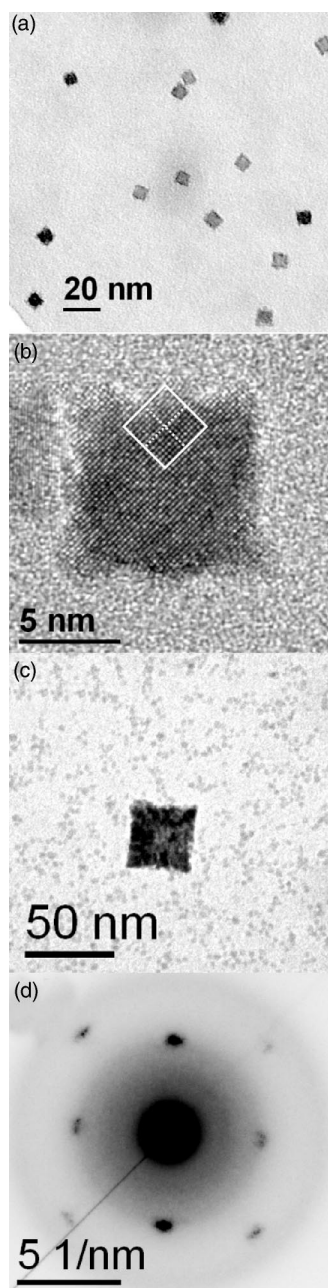


FIG. 1. (a) TEM bright field picture of Mo nanoclusters deposited onto  $\text{Si}_3\text{N}_4$  membrane. (b) HRTEM image along the  $\langle 100 \rangle$  orientation, projection of rhombic dodecahedron is superimposed. (c) Large cuboidally shaped particle surrounded by noncubic small clusters of size  $\sim 4$  nm. (d) Selected area electron diffraction from the large cuboid in (c) splitting of (110) peaks due to self-assembly.

As Fig. 1(b) shows, the Mo cluster viewed along the  $\langle 100 \rangle$  projection appears to have a square shaped crystal habit, which could be the two-dimensional projection of a cuboctahedron or a cuboidally shaped particle. The uniform size distribution, as shown for example in Fig. 1(a), is required for self-assembly if this is to decrease the surface energy. Assuming a Wulff construction with the minimum radial distance to every face proportional to the corresponding surface energy, for the cube particle the surface energies for the facets (100) and (110) should obey the constraint  $\gamma_{100}/\gamma_{110} \leq 1/\sqrt{2}$ .<sup>5</sup> However, calculations for bcc Mo have shown ratios  $\gamma_{100}/\gamma_{110} \approx 1.45$ ,<sup>13</sup> which imply untruncated rhombic dodecahedron or  $\gamma_{100}/\gamma_{110} \geq \sqrt{2}$ .<sup>5</sup> Nonetheless the shape of the crystal habit can also be determined by kinetics,

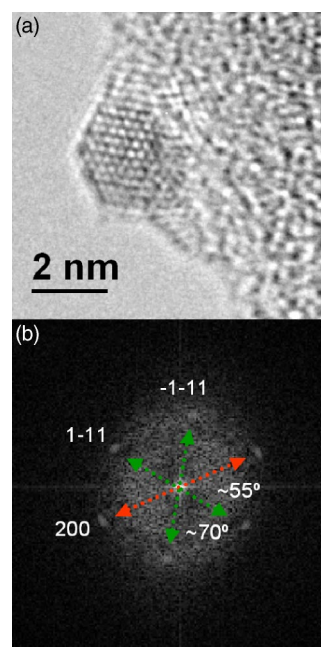


FIG. 2. (a) TEM image of a small cluster approximately 2.5 nm in size. (b) Characteristic angles of a fcc structure in the power spectra.

where if the growth of the (100) facet is faster than that of the (110), then the resulting particle will be cuboidally shaped. The presumption of a cuboidal shape is supported by the measurement of the phase change of the object wave by electron holography, which has been successfully applied in the analysis of nanoparticle shapes.<sup>14</sup> In the absence of any electric and magnetic field in the sample and neglecting dynamical diffraction effects,<sup>15</sup> the phase change is given by  $\Delta\Phi = C_E \cdot V_0 \cdot t$ , where  $C_E = 7.28 \cdot 10^6 \text{ m}^{-1} \text{ eV}^{-1}$  for 200 kV electrons,  $V_0$  is the mean inner crystal potential in units of eV and  $t$  is the object thickness in units of meter. The phase change is therefore linearly dependent on object thickness. The reconstructed phase from an electron hologram is shown in Fig. 3. The nearly constant phase in the projected object reconstructed from holograms acquired in several orientations close to  $\langle 100 \rangle$  zone axis in order to minimize dynamical diffraction effects excludes a cuboctahedral crystal habit.

On closer inspection of the Mo particles in Figs. 1(b) and 1(c) it is clear that the apparent cubes have malformed edges, which indicates that the building block or unit Mo

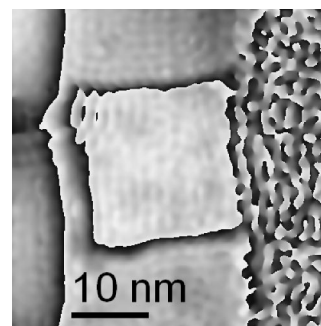


FIG. 3. Phase change within a Mo cluster of a size 20 nm lying on a  $\text{Si}_3\text{N}_4$  membrane reconstructed from an electron hologram demonstrating nearly constant thickness in projected direction. The hologram taken at biprism voltage adjusted to give 0.5 nm fringes was recorded on a  $1\text{k} \times 1\text{k}$  Gatan multiscan 794IF CCD camera. The phase was reconstructed using the HoloWorks© (Ref. 19) software package.

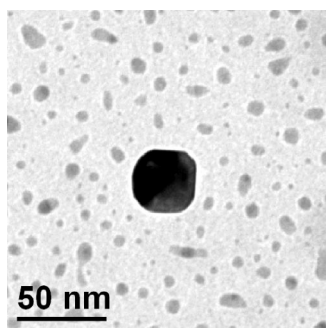


FIG. 4. TEM image of a large particle surrounded by smaller clusters after high temperature annealing at 900 °C.

particle can have a shape other than a cube, or that the stacking of cube particles is rather imperfect. The latter case can be excluded since in this case the self-assembly is unlikely to lead to any significant surface energy minimization. Notably, Fig. 1(c) shows a large particle within a “sea” of small bcc Mo particles. In this case, the presence of self-assembled cuboids further supports the possibility that the basic unit particles that constitute the larger Mo cube particles are not necessarily cubes themselves. The structural unit particle that forms the building block of the larger cuboids is more likely a rhombic dodecahedron. The latter is the stable form of an isolated bcc Mo particle and it leads to ledges along the particle sides as in Fig. 1(b).

Annealing of the cuboids leads to alteration of the crystal habit (Fig. 4) as was also observed for Fe clusters in previous studies.<sup>16</sup> The rounded shape of the Mo nanoclusters for the large Mo cuboids can be thought to be that of a truncated rhombic dodecahedron with the facet corners rather blurred. Annealing also results in coalescence of clusters at temperatures around 800 °C, which is approximately 1/3 the melting temperature of bulk Mo (2623 °C). The rounded shape of the clusters after coalescence indicates that truncation of the initial cuboidal shape became more favorable,<sup>4,17,18</sup> i.e., {100} became more stable. Besides faceting, which slows coalescence, cluster oxidation during annealing can inhibit coalescence,<sup>18</sup> which is not the case here since the Mo nanoclusters do not oxidize.

In conclusion, Mo clusters with sizes 4 nm or larger show a body-centered crystal structure with a distorted cubic habit. The Mo nanoclusters self-assemble into larger distorted cuboids, without developing any oxide shell upon ex-

posure to air. With reducing cluster size to  $\leq 3$  nm, the fcc structure appears due to dominance of surface energy minimization, while self-assembly into large cuboids of  $\sim 30$  nm is still observed. Our observations indicate that the basic structural units of these large cuboids are not smaller particles of a cubic shape but likely of the rhombic dodecahedron type. Annealing of the clusters leads to their coalescence at high temperatures of approximately 800 °C, with the crystal habit changing to truncated rhombic dodecahedron for isolated clusters. The truncation is more pronounced upon increasing annealing temperature and time, leading to particles with a shape corresponding to truncated rhombic dodecahedron.

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